

## BATCH PROCESS FOR PREPARING PULP

### FIELD OF THE INVENTION

The present invention relates to a process for preparing kraft pulp in which lignocellulosic material is treated with recycled process liquors, polysulfide and fresh re-causticized white liquor for removing lignin therefrom. More particularly, the present invention relates to the use of polysulfide white liquor (or another polysulfide source) in the early stages of modern displacement kraft batch cooking, and the advantage thereof in terms of improved pulp yield.

### BACKGROUND OF THE INVENTION

In the various kraft pulping processes, lignocellulosic material, most commonly wood chips, is generally treated at elevated temperatures with alkaline cooking liquor containing sodium hydroxide and sodium hydrogen sulfide, called white liquor. In these processes a significant part of the cellulosic material, especially hemicelluloses, are partly lost due to reactions with the white liquor. In kraft pulping conditions hemicelluloses undergo alkaline peeling reactions, de-polymerization, in which the hemicelluloses are dissolved as organic acids into the cooking liquor. A known fact is that by a polysulfide treatment, hemicelluloses are stabilized and are thereafter more resistant to cooking liquor in kraft cooking conditions, which leads to higher yield from the processes lignocellulosic substance input.

In kraft pulping processes, fresh cooking liquor is obtained from the recovery furnace's inorganic smelt, which is dissolved in water and causticized to produce white liquor.

Polysulfide-containing white liquor is obtained from causticized white liquor by various processes, which partially oxidize the liquor's sodium sulfide into polysulfide. These processes typically use oxidation catalysts to polymerize the white liquor's hydrogen sulfide. Also, polysulfide can be produced directly by elemental sulfur addition into white liquor. Polysulfide-containing white liquor is called polysulfide white liquor or orange liquor.

The use of polysulfide white liquor has been quite straightforward in conventional kraft cooking operations. The normal white liquor has been converted to polysulfide white liquor, and that liquor has been used in the same manner as normal white liquor. After the  
5 impregnation into the wood chips in the digester and during the temperature rise to above 100 °C, the polysulfide has reacted with the carbohydrates making them less vulnerable to alkaline degradation. Later during the cook, when temperature has risen over 140 °C, the rest of the polysulfide has rapidly broken down through thermal decomposition. As all the conventional cooking systems have used cooking liquors having initial temperatures well  
10 below 100 °C and the temperature in the digester has been elevated slowly or in steps, the polysulfide has had the possibility to react and facilitate higher pulp yield.

However, the development of the batch cooking systems has caused a major deviation from the conventional cooking technology: White liquor is introduced into the digester as “hot  
15 white liquor”, which has been heated up using the heat of the previously generated spent liquor, and steam. For the purpose of this disclosure, “hot” is meant to designate a liquor having a temperature above its boiling point at ambient pressure, i.e. a liquor that must be stored in a pressurized vessel.

20 The hot white liquor temperature in typical displacement batch cooking is 140 – 180 °C. From the displacement batch process point of view, polysulfide has been an impossible chemical. Polysulfide is unstable at higher temperatures, for instance at those used in kraft cooking; the chemical begins to break down at temperatures above 100°C, and it degrades completely in a few minutes at 150 °C. Thus at the typical process temperature of the hot  
25 white liquor, polysulfide white liquor is not stable at all. This fact has disabled the use of polysulfide in the modern displacement kraft pulping processes developed for higher energy and chemical economy and improved pulp quality.

During the early 80's, new energy efficient kraft batch processes using various liquor  
30 displacements emerged. Characteristic for the displacement kraft batch process is to recover hot black liquor from the end of the cooking by displacement and then re-use the energy in the subsequent batches. Partly this is done by using the hot spent cooking liquor as such,

and partly by heating the white liquor with the heat of the hot spent liquor leaving the digester system or collected for re-use at low temperature. This process arrangement leads to high temperatures in the input liquor accumulators. A low temperature white liquor, typically at 80 °C in the storage tank after re-causticization, cannot be used anymore, and  
5 the environment for stable polysulfide in the white liquor does not exist anymore.

Good examples of the development of displacement batch processes are given in, e.g., Fagerlund, U.S. Pat 4,578,149 and Östman, U.S. Pat 4,764,251. A further characteristic feature of a modern displacement batch process is to combine energy efficiency and  
10 efficient use of residual and fresh cooking chemicals to achieve, in addition to energy efficiency, high pulp strength and good delignification through hydroxyl and hydrosulfide concentration and temperature profiling at different stages of the cooking cycle (Hiljanen, Tikka, EP-B 520 452, Tikka, U.S. Pat 5,183,535).

15 The strive for higher pulp yield is easy to understand. It is always more profitable to produce more pulp from a certain wood amount. The pulping industry has faced increasing environmental pressure to radically cut down environment-polluting effluents. Reduction of the organic effluents from pulp bleaching requires kraft cooking to be extended to yield much lower residual lignin concentration in the pulp than before. Extended cooking means  
20 more carbohydrate losses. In order to enable extended cooking while improving energy economy and pulp quality, one popular option for the industry has been to use modern displacement batch cooking technology. In spite of all the advantages of this technology, it has not been possible to take the pulp yield advantage by using polysulfide white liquor. The present invention overcomes these problems and enables an efficient use of polysulfide  
25 by a novel displacement batch cooking process.

The use of anthraquinone (AQ) as a cooking catalyst is well known. It acts by reducing carbohydrate end groups, stabilising them against alkaline peeling and producing anthrahydroquinone, which is alkali soluble. Anthrahydroquinone reduces lignin, making it  
30 more reactive. In this process, anthraquinone is formed again and may react with carbohydrates.

During operation of displacement batch cooking processes, it has been observed that the properties of the black liquor originating from the early stages of the cook differ from those of black liquor from a traditional cook. Recycled black liquor originating from the early stages of the cooking sequence may complicate the evaporation of black liquor. A particular problem is fouling of the surfaces of heat exchangers in the evaporation plant, leading to a decrease in heat transfer. These evaporator fouling problems are typically related to calcium. In the early stage of alkaline cooking, calcium-containing material dissolves into the black liquor from the lignocellulosic material. In a traditional cook, the cook proceeds with heating, the temperature increases and no essential liquor exchange occurs. Then, a major part of the dissolved calcium-containing material in the cooking liquor is broken down, calcium carbonate is formed and as a result, a major part of the calcium is resorbed onto the lignocellulosic material in the digester. Following such a cooking process, evaporation of the black liquor can normally be carried out without problems caused by precipitation of calcium. In contrast, the evaporation problems with black liquors originating from the early stages of cooking are typically related to calcium-containing material dissolved in the early stages of a cook. The dissolved calcium-containing material has not been degraded, and the amount of calcium bound to the dissolved material in the black liquor is high. As disclosed in publication EP 1 242 674, this problem may be solved by re-introducing liquor having a high calcium precipitating potential into the digester as a displacement liquor at the end of a cook. At this point, the digester temperature is sufficiently high to cause calcium liberation. The calcium is then removed together with the pulp, and does not enter the evaporation and regeneration cycle.

## 25 SUMMARY OF THE INVENTION

In accordance with the present invention, a method for producing pulp using polysulfide white liquor has been provided. The method involves a kraft batch process which comprises the addition of polysulfide white liquor in the impregnation and pretreatment in the very 'front-end' of the cooking process, and a finalizing delignification stage with white liquor and optional cooking catalyst addition, which is facilitated by the modified 'front-end' process chemistry resulting in improved pulp yield. A volume of polysulfide white liquor is added as the first portion of liquor to enter the digester, or admixed with the

impregnation liquor prior to this being pumped into the digester. For the purpose of this disclosure, "impregnation liquor" means a liquor stored at a temperature below its atmospheric boiling point, used for a first immersion of the lignocellulosic raw material in a batch pulping process.

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In the present invention, lignocellulosic material entering a displacement batch process is thus pretreated with polysulfide- containing process liquors in conditions favourable for pre-treatment and polysulfide stability. A set of displacement batch process arrangements, capable of taking advantage of the polysulfide white liquor, are presented. The required  
10 dose of fresh polysulfide white liquor is introduced in the initial stage of the process. The impregnation stage provides for both impregnation and polysulfide pre-treatment reactions. An impregnation liquor circulation collects the displaced impregnation liquor which is re-used to fill and pressurize the digester after the first fresh liquor fill. As a result, the polysulfide concentration and dosage remain at a high level, and only the liquor balance  
15 excess is left over to be sent to chemicals recovery or re-use later in the cooking sequence. The displacement cooking process sequence then continues with hot fills of black and white liquors, cooking and final displacement.

An optional feature in the present invention is a new way to use a cooking catalyst, such as  
20 anthraquinone (AQ). As the generation of polysulfide white liquor decreases the concentration of hydrosulfide ions, the delignification rate is slower, reducing cooking capacity. The cooking catalyst can be used to maintain a normal kraft cooking rate and production level. In the present invention, the catalyst may be introduced into the digester together with the hot white liquor. By this means it will not escape due to displacements,  
25 and on the other hand, it arrives in the hot cooking stage where it is most needed. As a result, the technical and economical benefits of the displacement batch cooking are retained, while the advantages of polysulfide and cooking catalyst can be fully exploited.

#### BRIEF DESCRIPTION OF THE FIGURES

30 Figure 1 shows a block diagram of a kraft displacement batch cooking system according to the invention. The top of the figure defines the required tanks, leaving or entering streams denoted by letters. The cooking stage sequence is displayed therebelow, chronologically

starting from the top and the vertically indicated streams representing the liquors passing through the digester during the various stages. The letters denoting the various entering and leaving streams correspond to the source or destination in the tank scheme.

- 5 Figure 2 shows a further embodiment of a kraft displacement batch cooking system according to the invention.

#### DISCLOSURE OF THE INVENTION

- 10 In the following, the method of the invention is disclosed in detail with reference to the attached Figure 1. It is understood, that liquor is charged from the digester bottom and displaced gases and liquor leave from the top.

The kraft batch cook is started by charging the digester with wood chips, or with another lignocellulosic material. After the lignocellulosic material charge, the digester is filled in a  
15 stepwise sequence using a volume of fresh polysulfide white liquor X1 from polysulfide white liquor tank 6, and impregnation liquor A1 from tank 4, topping the digester full of liquor. The volume of polysulfide white liquor may be added as a separate first portion, forming a raising pad of liquor as further liquor is pumped in from below. Alternatively, the polysulfide white liquor is mixed into the impregnation liquor.

- 20 An overflow, A2, conducted to the impregnation liquor tank 4, is preferred in order to remove air and the diluted first front of liquor. After the flow A2 is stopped, the digester is pressurized and impregnation is completed during an appropriate period of time. The cooking process is then continued by pumping in a volume of hot black liquor B1 from hot  
25 black liquor accumulator 1. The cooler impregnation liquor A3, displaced by hot black liquor, is conducted to impregnation liquor tank 4 to be re-used in subsequent batches. Pumping a volume C of hot white liquor from tank 3 into the digester then continues the cooking sequence. Together with white liquor C, an amount of cooking catalyst may be dosed into the digester. The liquor D1, displaced by hot liquor above about the atmospheric  
30 boiling point, is conducted to hot black liquor accumulator 2.

At the end of the sequence described above, the digester is close to the final cooking temperature. The final heating-up is carried out using direct or indirect steam heating and digester re-circulation. After the desired cooking time when the delignification has proceeded to the desired final reaction degree, the spent liquor is ready to be displaced with wash filtrate E1 from tank 5. A volume A4 from impregnation liquor tank 4 may be used as a first portion of displacement liquor in order to deactivate the potential scale-forming calcium therein, as disclosed in EP 1 242 674.

In the final displacement, the first displaced volume B2 displaced by wash filtrate is conducted to black liquor accumulator 1. The second portion D2 of displaced black liquor, which is diluted by the wash filtrate but is still above atmospheric boiling point, is conducted to the hot black liquor accumulator 2. After completed final displacement, the digester contents are discharged for further processing of the pulp. The above cooking sequence may then be repeated.

The hot black liquor from accumulator 2 is conducted to the evaporation plant, first being used to heat white liquor due for tank 3, and/or water, by means of heat exchange.

Tank 6 is provided for storage of polysulfide white liquor, supplied from a plant for polysulfide generation.

#### DESCRIPTION OF PREFERABLE EMBODIMENTS

In the following, reference is made to the figure described in the preceding section.

In the process of the present invention, a volume of polysulfide white liquor, corresponding to 25-90 % of the total active alkali dosage and resulting in 0,5% to 5% polysulfide dosage on abs. dry wood is added into the digester before the impregnation fill is completed. Impregnation is carried out using temperature of between 70 °C and 120 °C, preferably between 85 - 95 °C, and a time of between about 20 to about 120 minutes, preferably between about 30 to about 60 minutes, more preferably between about 25 to about 40 minutes.

In a preferable embodiment, the polysulfide white liquor is added as a separate portion before the introduction of further liquor.

- 5 In a preferable embodiment, the volume of polysulfide white liquor corresponds to 50-75 % of the total active alkali dosage for the relevant batch.

In accordance with a particular embodiment of the process of the present invention, a cooking catalyst is used. Preferable catalysts are anthraquinone, anthraquinone sulfonate,  
10 and hydroanthraquinone. Any other appropriate redox-catalyst as anticipated by those skilled in the art may be used.

In accordance with an alternative embodiment of the process of the present invention, the following fractions displaced from the digester:

15 - hot cooking spent liquor fraction B2 and  
- fractions D1 and D2, which are of lower temperature and poorer in chemicals,  
are collected in a single accumulator to be used in the hot black liquor pretreatment stage. In this configuration, hot black liquor accumulators 1 and 2 of Figure 1 are combined. The black liquor flow to the evaporation plant is drawn from the single hot black liquor  
20 accumulator, the stream being used to heat, by means of heat exchange, white liquor heading for white liquor accumulator 3, and/or water, as shown for tank 2 in Fig 1.

If high dosages of polysulfide white liquor are used in the impregnation stage of the process, longer impregnation times than in the prior art and/or a two accumulator system  
25 and/or impregnation liquor transfer to hot black liquor tank 1 may be used in order to avoid too high a residual alkali concentration in the feed of the evaporation plant. Thus, in accordance with a further embodiment of the process of the present invention, shown in Figure 2, a volume of impregnation liquor from impregnation tank 4 is conducted to hot black liquor tank 1 to be used in hot black liquor treatment, B1. The stream from  
30 impregnation liquor tank 4 to hot black liquor tank 1 may be heated by means of heat exchange with the stream from hot black liquor accumulator 2 to the evaporation plant.



In addition to the white liquor charge prior to the cooking stage, one or more additional white liquor charges may be carried out during the cook.

5 The principal advantage of the process of the present invention is that the 'front-end' of the kraft displacement batch cooking system is rendered more effective from a chemical point of view, and in regard to process arrangements. The polysulfide charge used reflects the improvement in pulp yield from the digested lignocellulosic material.

10 The following examples are illustrative of the invention. The following abbreviations are used:

|        |                                   |
|--------|-----------------------------------|
| WBL    | Warm impregnation black liquor    |
| DWBL   | Displaced WBL (from the digester) |
| 15 HBL | Hot black liquor                  |
| RHBL   | Displaced HBL (from the digester) |
| DCBL   | Displaced cooking black liquor    |
| WF     | Wash filtrate                     |
| PSWL   | Polysulfide white liquor          |

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Production of a normal 'reference' pine kraft pulp using the displacement kraft batch technique:

4,0 kg pine (*Pinus sylvestris*) chips (oven dry basis) were metered into a chip basket positioned in a 20-litre jacketed displacement batch digester. The lid of the digester was closed. Impregnation black liquor, consisting of wash filtrate and white liquor (WBL, 80-90°C, 25 gEA/l) was pumped in during app. 10 minutes followed by impregnation at 90°C under 2,5 bar overpressure. The duration of the impregnation stage was 40 minutes (WBL-fill and impregnation in total). After impregnation, a hot black liquor pre-treatment stage was commenced by introducing hot black liquor (HBL 1, 150°C, app. 20 gEA/l) to the bottom of the digester, displacing the spent impregnation liquor (DWBL) out from the top of the digester. The hot black liquor pre-treatment stage duration was 30 minutes. After hot black liquor pre-treatment stage, hot white liquor (121 gEA (NaOH)/l, sulfidity 37%)

charge was introduced into the digester bottom displacing the corresponding volume of spent hot black liquor (RHBL) out of the digester. A 45 minute heat-up sequence with cooking liquor circulation raised the temperature from 150°C to the cooking temperature of 167°C. At 250 H-factors, a white liquor charge was introduced into the digester bottom displacing the corresponding volume of spent hot black liquor out of the digester (DCBL 1). After the cooking time fulfilled the target H-factor, terminal displacement was started by introducing cool DWBL and wash filtrate (WF) in a sequence into the digester bottom displacing the hot spent black liquor out of the digester top (DCBL 2). The first displaced portion the hot black liquor with the hot black liquor, displaced earlier during the cooking sequence (DCBL 2 + DCBL 1) covered the volume needed for the next cook's hot black liquor (HBL 1). The terminal displacement stage duration was approximately 40 minutes. After the terminal displacement, the pulp was disintegrated, washed with deionised water, screened and analysed. The cooking procedure was repeated and thus equilibrium in the cooking process was obtained and the cooks started to repeat themselves corresponding to the industrial batch cooking system.

The experimental set-up to produce pulp according to the invention is described below.

4,0 kg pine (*Pinus sylvestris*) chips (oven dry basis) were metered into a chip basket positioned in a 20-litre jacketed displacement batch digester. The lid of the digester was closed. The chips were steamed until the digester temperature was 100°C, approximately 5 minutes. Impregnation liquors were introduced as sequence as follows: initially polysulfide white liquor black liquor (PSWL, volume according to the charge, app. 4,5-5l); subsequently re-circulated spent impregnation liquor (DWBL) to hydraulically fill the digester. The impregnation fill sequence took app. 11-13 minutes and was followed by impregnation at 90°C under 2,5 bar overpressure. The duration of the impregnation stage was 40 minutes (fill sequence and impregnation in total). After impregnation, a hot black liquor pre-treatment stage was carried out by introducing hot black liquor (HBL 1, 150°C, app. 20 gEA/l) to the bottom of the digester of the digester, displacing the spent impregnation liquor from the top of the digester (DWBL). The hot black liquor pre-treatment stage duration was 30 minutes. After the hot black liquor pre-treatment stage, hot white liquor (121 gEA (NaOH)/l, sulfidity 37%) charge was introduced, displacing the

corresponding volume of spent hot black liquor from the digester (RHBL). Together with the WL, a cooking catalyst was charged mixed with a small volume of hot black liquor. A 45 minute heat-up sequence with cooking liquor circulation raised the temperature from 150°C to the cooking temperature of 167 °C. At 250 H-factors, a further white liquor charge was introduced into the digester bottom displacing the corresponding volume of spent hot black liquor from the digester (DCBL 1). After the cooking time fulfilled the target H-factor, terminal displacement was started by introducing a volume of cool DWBL and wash filtrate (WF) in a sequence into the digester bottom displacing the hot spent black liquor out of the digester top (DCBL 2). The first displaced portion of hot black liquor together with the hot black liquor displaced earlier during the cooking sequence (DCBL 2 + DCBL 1) covered the 17 l volume needed for the next cook's hot black liquor (HBL 1). After the terminal displacement, the pulp was disintegrated, washed with deionised water, screened and analysed. The cooking procedure was repeated, equilibrium in the cooking process was reached and the cooks started to repeat themselves corresponding to the industrial batch cooking system.

#### Example 1. Demonstration of yield improvement using polysulfide white liquor addition

The reference cook follows the same addition and temperature sequences as the cooks according to the invention. All cooks were digested to the same target kappa number. A clear yield improvement correlating with polysulfide addition can be observed

| Cooking model | PS-charge, % |              | Total yield, %<br>on wood | Rejects, % on<br>wood |
|---------------|--------------|--------------|---------------------------|-----------------------|
|               | on wood      | Kappa number |                           |                       |
| Reference     | Nil          | 25,9         | 44,0                      | 0,26                  |
| SB-PSAQ       | 1,21         | 25,9         | 45,8                      | 0,36                  |
| SB-PSAQ       | 1,58         | 25,8         | 46,8                      | 0,24                  |

Example 2. The effect of anthraquinone to preserve the rate of delignification during cooking

It is seen, that the reference cook requires a significantly higher H-factor to reach the target kappa number.

| Method           | PSWL      |               | H-factor | EoC, g/l | Kappa# | Reject,          |           |
|------------------|-----------|---------------|----------|----------|--------|------------------|-----------|
|                  | in imp, % | PS, % on wood |          |          |        | Yield, % on wood | % on wood |
| Reference        | -         | -             | 1285     | 16       | 26,9   | 43,6             | 1,01      |
| PS pad, AQ 0%    | 70 %      | 1,45          | 1106     | 19,1     | 27,1   | 44,3             | 0,15      |
| PS pad, AQ 0,05% | 70 %      | 1,45          | 1030     | 19,9     | 26,7   | 44,5             | 0,16      |
| PS pad, AQ 0,1%  | 70 %      | 1,45          | 1096     | 18,1     | 27,3   | 45,8             | 0,1       |